



(19) Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number: 0 668 342 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 95200281.4

(51) Int. Cl.: C10G 65/04

(22) Date of filing: 06.02.95

(30) Priority: 08.02.94 EP 94400286

(43) Date of publication of application:
23.08.95 Bulletin 95/34

(84) Designated Contracting States:
DE FR GB IT NL

(71) Applicant: SHELL INTERNATIONALE
RESEARCH MAATSCHAPPIJ B.V.
Carel van Bylandtlaan 30
NL-2596 HR Den Haag (NL)

(72) Inventor: Eilers, Jacobus c/o Shell Nederland
Raffin. B.V.
Department RT/109
Vondelingenweg 601
NL-3196 KK Vondelingenplaats Rotterdam
(NL)
Inventor: Gilson, Jean-Pierre
Route de Caen
F-76530 Grand Couronne (FR)
Inventor: Hoek, Arend
Badhuisweg 3
NL-1031 CM Amsterdam (NL)
Inventor: Posthuma, Sytze Abel
Carel van Bylandtlaan 30
NL-2596 HR The Hague (NL)

(54) Lubricating base oil preparation process.

(55) A process for the preparation of lubricating base oils comprising subjecting a waxy raffinate to a pour point reducing treatment, and recovering lubricating base oil therefrom, which waxy raffinate has been prepared by contacting a hydrocarbon product with hydrogen in the presence of a hydroconversion catalyst, comprising a catalytically active metal having hydrogenation/dehydrogenation activity supported on a refractory oxide carrier, under conditions such that hydrocracking and hydroisomerisation of the hydrocarbon product occur to yield the waxy raffinate, wherein the hydrocarbon product has been prepared by:

(a) contacting a mixture of carbon monoxide and hydrogen with a hydrocarbon synthesis catalyst at elevated temperature and pressure to prepare a substantially paraffinic hydrocarbon wax; and

(b) contacting the hydrocarbon wax so-obtained with hydrogen in the presence of a hydrogenation catalyst under conditions such that substantially no isomerisation or hydrocracking of the hydrocarbon wax occurs to yield the hydrocarbon product.

EP 0 668 342 A1

The present invention relates to a process for the preparation of lubricating base oils, in particular the preparation of very high viscosity index lubricating base oils from a mixture of carbon monoxide and hydrogen.

The term "very high viscosity index" refers to a viscosity index (VI) above 135, as determined by 5 ASTM-D-2270.

The preparation of hydrocarbons from a mixture comprising carbon monoxide and hydrogen by contacting the mixture with a suitable synthesis catalyst at elevated temperatures and pressures is known in the art as the Fischer-Tropsch synthesis. It is known in the art to apply Fischer-Tropsch synthesis processes in the preparation of a range of principally aliphatic hydrocarbons having a wide range of 10 molecular weights.

In order to improve the yield of valuable hydrocarbon products from the Fischer-Tropsch synthesis process, a variety of process schemes have been proposed for upgrading the Fischer-Tropsch products. Thus, in US patent No. 4 125 566 a process scheme is disclosed in which the highly olefinic effluent of a 15 Fischer-Tropsch synthesis is treated by one or more of distillation, polymerisation, alkylation, hydrotreatment, cracking-decarboxylation, isomerisation and hydroreforming. This process scheme yields products lying mainly in the gasoline, kerosene and gasoil ranges.

From the variety of aforementioned processes which may be applied in upgrading the products of a Fischer-Tropsch synthesis, a number of process schemes have been proposed which rely upon the 20 application of hydrotreatment processes in the upgrading. Thus, US patent specification No. 4 478 955 discloses a process scheme comprising contacting the effluent of a Fischer-Tropsch synthesis process with hydrogen in the presence of a suitable hydrogenation catalyst. The effluent of the Fischer-Tropsch synthesis is described in this US patent specification as comprising pre-dominantly olefins and carboxylic acids. Under the action of the hydrogenation treatment, useful fuel components comprising alkanes, 25 alcohols and esters are produced.

In an alternative process scheme disclosed in US patent specifications Nos. 4 059 648 and 4 080 397, the products of a Fischer-Tropsch synthesis are upgraded by being subjected firstly to a hydrotreatment and thereafter fractionated. Selected fractions of the fractionated product are subsequently subjected to a 30 selective hydrocracking process in which the fractions are contacted with a special zeolite catalyst capable of transforming the aliphatic hydrocarbons present in the fractions into aromatic hydrocarbons. The resulting aromatic-rich products are said to be useful as gasoline and light and heavy fuel oils.

More recently, much interest has been paid to the application of the Fischer-Tropsch synthesis in the preparation of substantially paraffinic hydrocarbon products suitable for use as fuels. Whilst it is possible to 35 use the Fischer-Tropsch synthesis process to directly prepare paraffinic hydrocarbons having boiling points in the boiling point ranges of the fuel fractions, it has been found advantageous to use the Fischer-Tropsch synthesis process to prepare high molecular weight paraffinic hydrocarbons having a boiling point above the upper limit of the boiling point range of the middle distillates, that is a Fischer-Tropsch wax having a 40 boiling point above 370 °C, and subject the products so-obtained to a selective hydrocracking process to yield the desired hydrocarbon fuels.

Thus, in British patent specification No. 2 077 289, a process is disclosed comprising contacting a 45 mixture of carbon monoxide and hydrogen with a catalyst active in the Fischer-Tropsch synthesis and thereafter cracking the resulting paraffinic hydrocarbons in the presence of hydrogen to yield middle distillates. A similar process scheme is disclosed in European patent application No. 0 147 873.

European patent application No. 0 583 836 discloses a process for the preparation of hydrocarbon fuels from carbon monoxide and hydrogen.

Of particular interest, however, is the use of the Fischer-Tropsch synthesis to prepare hydrocarbons suitable for use as lubricating base oil or lubricating base oil precursor, such as a Fischer-Tropsch wax.

Processes for the preparation of very high viscosity index lubricating base oils from Fischer-Tropsch wax feed are known in the art. United States patent specification No. 4 594 172 describes the preparation of 50 very high viscosity index lubricating base oils by treating a C₁₀-C₁₉ fraction of a Fischer-Tropsch wax with an organic peroxide to yield a C₂₀⁺ oligomerised fraction and hydroisomerising that fraction over a platinum-containing silica-alumina catalyst.

European patent application No. 0 515 256 describes a process for the hydroisomerisation (hydroconversion) of Fischer-Tropsch waxes, using a catalyst containing zeolite Y. Upon solvent dewaxing of a fraction boiling above 380 °C a lubricating base oil is obtained having a VI of at least 130 and a pour point of at least -12 °C. As outlined in this patent application, the hydroisomerisation treatment can be preceded by a hydrogenation treatment to remove any unsaturated hydrocarbons and oxygenates from the Fischer-Tropsch wax.

European patent application No. 0 321 303 discloses the preparation of middle distillate products from Fischer-Tropsch wax by a hydroisomerisation (hydroconversion) treatment. At least a portion of the bottoms fraction from the hydroisomerisation zone is either (a) further processed in a second hydroisomerisation zone or (b) fractionated and/or dewaxed for the production of a lubricating oil fraction boiling in the range of 5 343.3 °C to 510 °C. If desired, oxygenates may be removed from the Fischer-Tropsch wax by distillation. The hydroisomerisation catalyst to be used in the first hydroisomerisation (hydroconversion) treatment is a platinum on fluorided alumina catalyst which is particularly effective (selective) at converting paraffinic Fischer-Tropsch wax to middle distillate material. In particular, this catalyst is reported to be more effective than a catalyst containing a zeolite, in particular zeolite beta, as described in Example 3 of this patent 10 application.

In contrast to this, the aforementioned European patent application No. 0 515 256 describes in Example 3 that a zeolite Y catalyst can be as effective (selective) in the preparation of middle distillates from Fischer-Tropsch wax as a platinum on silica-alumina catalyst, but that a zeolite Y catalyst is much more active. For a conversion of about 40% by weight of Fischer-Tropsch wax to products boiling below 400 °C, the zeolite 15 Y catalyst required a reactor temperature of 260 °C, whilst the platinum on silica-alumina catalyst required a reactor temperature of 340 °C.

A hydroisomerisation (or hydroconversion) process involves both hydrocracking of paraffinic hydrocarbons and isomerisation of linear paraffinic hydrocarbons to branched paraffinic hydrocarbons. If it is desired to prepare lubricating base oils, it is advantageous to minimize the hydrocracking activity and to maximize 20 the hydroisomerisation activity. Nevertheless, some hydrocracking activity is still required to crack the heaviest wax molecules to lower boiling products. A disadvantage of a highly active catalyst, such as a zeolitic catalyst like zeolite Y, is that normally the hydrocracking activity is still too high and the hydroisomerisation activity too low. As will be discussed hereinafter, other molecular sieve catalysts are known such as silicoaluminophosphates and other zeolitic catalysts wherein the activity (expressed in terms 25 of acidity) has been reduced to an alpha-value below 20 or even below 10 or 5. However, these catalysts normally do not have sufficient hydrocracking activity.

Thus, European patent application No. 0 464 547 describes a process for the preparation of high viscosity index lubricants from slack wax by a two-step process wherein the first step the slack wax is hydrocracked under mild conditions using an amorphous catalyst, in particular a catalyst comprising Ni and 30 W on a fluorided alumina carrier, and in the second step hydroisomerised using a low acidity zeolite beta catalyst, preferably having an alpha value of not greater than 5.

The alpha value is an approximate indication of the catalytic cracking activity of the catalyst compared to a standard catalyst. The alpha test gives the relative rate constant (rate of normal hexane conversion per volume of catalyst per unit time) of the test catalyst relative to the standard catalyst which is taken as an 35 alpha of 1 (Rate Constant = 0.016 sec⁻¹). The alpha test is described in United States patent specification No. 3 354 078 and in J. Catalysis, 4, 527 (1965); 6, 278 (1966); and 61, 395 (1980) and discussed in European patent application No. 0 464 547. The alpha value is determined on the catalyst carrier not containing any catalytically active metals.

For the purposes of this specification the term hydroconversion process as used hereinafter refers to a 40 process in which hydrocracking reactions and hydroisomerisation reactions occur and which is carried out in the presence of a catalyst comprising a refractory oxide carrier.

The term hydroisomerisation process as used hereinafter refers to a process in which hydroisomerisation reactions and hydrocracking reactions occur, but which is carried out after a hydroconversion treatment and in which process generally less hydrocracking occurs than in the hydroconversion process.

45 A disadvantage of hydroconversion catalysts comprising a refractory oxide carrier is the high operating temperature which is required, in particular if the catalyst has been used for a prolonged time such as more than 2 years. In order to compensate for any catalyst deactivation generally the reaction temperature is increased. Above 350 °C and in particular above 400 °C at least part of the Fischer-Tropsch wax is converted into undesired aromatic compounds. Accordingly, it would be desirable to be able to provide a process which allows a hydroconversion process to be carried out at an operating temperature well below 50 400 °C and preferably below 350 °C, whilst using a catalyst containing a refractory oxide carrier and a catalytically active metal having hydrogenation/dehydrogenation activity.

It has now surprisingly been found that if the Fischer-Tropsch wax (hydrocarbon wax) is first contacted 55 with hydrogen in the presence of a hydrogenation catalyst under conditions such that substantially no hydroisomerisation or hydrocracking of the hydrocarbon wax occurs, the hydroconversion process can be operated at a reaction temperature below 400 °C, and even below 350 °C, even after the hydroconversion catalyst has been used for a prolonged time, that is for example more than 2 years. As compared with a process in which the Fischer-Tropsch wax is contacted with a hydroconversion catalyst without a preceding

hydrogenation step, the reaction temperature can be at least 5 °C, preferably at least 10 °C lower.

Further, it has been found that the hydroconversion catalyst deactivates much slower in a process which involves a preceding hydrogenation step. Thus, the rate of reaction temperature increase required to compensate for any loss of catalyst activity can be much slower.

5 Further, most surprisingly, it has been found that the process involving a hydrogenation step and a hydroconversion step exhibits a higher selectivity to valuable hydrocarbons boiling in the lubricating base oil range, compared with a prior art process comprising only a hydroconversion step.

10 Therefore, the present invention relates to a process for the preparation of lubricating base oils comprising subjecting a waxy raffinate to a pour point reducing treatment, and recovering a lubricating base oil therefrom, which waxy raffinate has been prepared by contacting a hydrocarbon product with hydrogen in the presence of a hydroconversion catalyst, comprising a catalytically active metal having hydrogencation/dehydrogenation activity supported on a refractory oxide carrier, under conditions such that hydrocracking and hydroisomerisation of the hydrocarbon product occur to yield the waxy raffinate, wherein the hydrocarbon product has been prepared by:

15 (a) contacting a mixture of carbon monoxide and hydrogen with a hydrocarbon synthesis catalyst at elevated temperature and pressure to prepare a substantially paraffinic hydrocarbon wax; and
 (b) contacting the hydrocarbon wax so-obtained with hydrogen in the presence of a hydrogenation catalyst under conditions such that substantially no hydroisomerisation or hydrocracking of the hydrocarbon wax occurs to yield the hydrocarbon product.

20 For the purposes of this specification, conditions such that substantially no hydrocracking or hydroisomerisation occurs in step (b) of the process of the present invention are defined as such conditions that the conversion in step (b) of the fraction of the feed boiling above 370 °C in % by weight, to a fraction boiling below 370 °C, is less than 10%.

25 In the hydroconversion step conditions such that hydrocracking and hydroisomerisation of the hydrocarbon product occur are defined as such conditions that the conversion as defined hereinabove is at least 15%.

30 For the purposes of this specification, the term "substantially paraffinic" when used in connection with hydrocarbon wax refers to a hydrocarbon mixture comprising at least 70 %wt (% by weight) paraffins, preferably at least 80 %wt paraffins. Hydrocarbon wax produced by the process of this invention typically comprises at least 90 %wt paraffins, more typically at least 95 %wt paraffins.

35 In step (a) of the process of the present invention, a feed comprising a mixture of carbon monoxide and hydrogen is contacted at elevated temperature and pressure with a catalyst active in the synthesis of paraffinic hydrocarbons. Suitable processes for the preparation of the mixture of carbon monoxide and hydrogen are well known in the art and include such processes as the partial oxidation of methane, typically in the form of natural gas, and the steam reforming of methane. The relative amounts of carbon monoxide and hydrogen present in the feed may vary over a wide range and may be selected according to the precise catalyst and process operating conditions being employed. Typically, the feed contacting the catalyst comprises carbon monoxide and hydrogen in a hydrogen/carbon monoxide molar ratio of below 2.5, preferably below 1.75. More preferably, the hydrogen/carbon monoxide ratio is in the range of from 0.4 to 1.5, especially from 0.9 to 1.3. Unconverted carbon monoxide and/or hydrogen may be separated from the synthesis product and recycled to the inlet of the synthesis reactor.

40 Suitable catalysts for use in the synthesis of paraffinic hydrocarbons are known in the art. Typically, the catalyst comprises, as the catalytically active component, a metal from Group VIII of the Periodic Table of the Elements. Particular catalytically active metals from Group VIII include ruthenium, iron, cobalt and nickel. For the process of the present invention, a catalyst comprising cobalt as the catalytically active metal is preferred.

45 The catalytically active metal is preferably supported on a porous carrier. The porous carrier may be selected from any suitable refractory metal oxide or silicate or mixture thereof. Particular examples of preferred carriers include silica, alumina, titania, zirconia and mixtures thereof. Carriers comprising silica and/or alumina are especially preferred.

50 The catalytically active metal may be applied to the carrier by any of the techniques known in the art, for example comulling, impregnation or precipitation. Impregnation is a particularly preferred technique, in which the carrier is contacted with a compound of the catalytically active metal in the presence of a liquid, most conveniently in the form of a solution of the metal compound. The compound of the active metal may be inorganic or organic, with inorganic compounds being preferred, in particular nitrates. The liquid employed may also be either organic or inorganic. Water is a most convenient liquid.

55 The amount of catalytically active metal present on the carrier is typically in the range of from 1 to 100 parts by weight, preferably 10 to 50 parts by weight, per 100 parts by weight of carrier material.

The catalytically active metal may be present in the catalyst together with one or more metal promoters or co-catalysts. The promoters may be present as metals or as the metal oxide, depending upon the particular promoter concerned. Suitable metal oxide promoters include oxides of metals from Groups IIA, IIIB, IVB, VB or VIB of the Periodic Table, oxides of the lanthanides and/or the actinides. Preferably, the catalyst comprises an oxide of an element in Group IVB of the Periodic Table, in particular titanium or zirconium. Catalysts comprising zirconium are especially preferred. As an alternative or in addition to the metal oxide promoter, the catalyst may comprise a metal promoter selected from Groups VIIIB and/or VIII of the Periodic Table. Preferred metal promoters include platinum and palladium. A most suitable catalyst comprises cobalt as the catalytically active metal and zirconium as a promoter. The promoter may be incorporated in the catalyst using any of the methods discussed hereinbefore with respect to the catalytically active component.

The promoter, if present in the catalyst, is typically present in an amount of from 1 to 60 parts by weight, preferably from 2 to 40 parts by weight, per 100 parts by weight of carrier material.

The hydrocarbon synthesis is conducted under conditions of elevated temperature and pressure. Typically, the synthesis is effected at a temperature in the range of from 125 to 300 °C, preferably from 175 to 250 °C. The reaction pressure is typically in the range of from 5 to 100 bar, preferably from 12 to 50 bar. The synthesis may be conducted using a variety of reactor types and reaction regimes, for example in a fixed bed regime, a slurry phase regime or an ebullating bed regime.

The hydrocarbon wax of the synthesis step (a) is subjected to a hydrogenation treatment in step (b) of the process of the present invention. The entire effluent of the synthesis stage may be led directly to the hydrogenation step. However, it is preferred to separate from the hydrocarbon wax of the synthesis stage unconverted carbon monoxide and hydrogen and water formed during the synthesis. If desired, the low molecular weight products of the synthesis stage, in particular the C₄- fraction, for example methane, ethane and propane, may also be removed prior to the hydrogenation treatment. The separation is conveniently effected using distillation techniques well known in the art. Alternatively, the hydrocarbon wax can be separated into a low boiling fraction, boiling for example below 330 °C or below 370 °C and at least one high boiling fraction, boiling above 330 °C or above 370 °C and treat the high boiling fraction in the process of the present invention. Separation may be effected using vacuum distillation or alternatively short path distillation such as vacuum film distillation (using wiped film evaporators).

In the hydrogenation stage, stage (b), the hydrocarbon product is contacted with hydrogen in the presence of a hydrogenation catalyst. Suitable catalysts for use in this stage are known in the art. Typically, the catalyst comprises as catalytically active component one or more metals selected from Groups VIB and VIII of the Periodic Table of Elements, in particular one or more metals selected from molybdenum, tungsten, cobalt, nickel, ruthenium, iridium, osmium, platinum and palladium. Preferably, the catalyst comprises one or more metals selected from nickel, platinum and palladium as the catalytically active component.

A particularly suitable catalyst comprises nickel as a catalytically active component.

Catalysts for use in the hydrogenation stage typically comprise a refractory metal oxide or silicate as a carrier. Suitable carrier materials include silica, alumina, silica-alumina, zirconia, titania and mixtures thereof. Preferred carrier materials for inclusion in the catalyst for use in the process of this invention are silica, alumina, silica-alumina, and diatomaceous earth (kieselguhr).

The catalyst may comprise the catalytically active component in an amount of from 0.05 to 80 parts by weight, preferably from 0.1 to 70 parts by weight, per 100 parts by weight of carrier material. The amount of catalytically active metal present in the catalyst will vary according to the specific metal concerned. One particularly suitable catalyst for use in the hydrogenation stage comprises nickel in an amount in the range of from 30 to 70 parts by weight per 100 parts by weight of carrier material. A second particularly suitable catalyst comprises platinum in an amount in the range of from 0.05 to 2.0 parts by weight per 100 parts by weight of carrier material.

Suitable catalysts for use in the hydrogenation stage of the process of this invention are available commercially, or may be prepared by methods well known in the art, for example the methods discussed hereinbefore with reference to the preparation of the hydrocarbon synthesis catalyst.

In the hydrogenation stage, the hydrocarbon wax is contacted with hydrogen at elevated temperature and pressure. The operating temperature may typically range from 100 to 300 °C, more preferably from 150 to 275 °C, in particular from 175 to 250 °C. Typically, the operating pressure ranges from 5 to 150 bars, preferably from 10 to 50 bars. Hydrogen may be supplied to the hydrogenation stage at a gas hourly space velocity in the range of from 100 to 10000 Nl/l/hr, more preferably from 250 to 5000 Nl/l/hr. The hydrocarbon wax being treated is typically supplied to the hydrogenation stage at a weight hourly space velocity in the range of from 0.1 to 5 kg/l/hr, more preferably from 0.25 to 2.5 kg/l/hr. The ratio of hydrogen

to hydrocarbon wax may range from 100 to 5000 Ni/kg and is preferably from 250 to 3000 Ni/kg.

The hydrogenation stage is operated under conditions such that substantially no isomerisation or hydrocracking of the feed occurs. The precise operating conditions required to achieve the desired degree of hydrogenation without substantial hydrocracking or hydroisomerisation occurring will vary according to the composition of the hydrocarbon wax being fed to the hydrogenation stage and the particular catalyst being employed. As outlined hereinbefore, as a measure of the severity of the conditions prevailing in the hydrogenation stage and, hence, the degree of hydrocracking and isomerisation occurring, the degree of conversion of the feed hydrocarbon may be determined. In this respect, conversion, in percent, is defined as the percent weight of the fraction of the feed boiling above 370 °C which is converted during the hydrogenation to a fraction boiling below 370 °C. The conversion of the hydrogenation stage is below 10%, preferably below 8%, more preferably below 5%.

In the process of the present invention, the hydrocarbon product leaving the hydrogenation stage substantially consists of high molecular weight, paraffinic hydrocarbons having a boiling point range within and above that of lubricating base oils. Lubricating base oils typically have a 5% by weight boiling point of at least 330 °C, preferably at least 370 °C. The boiling point range of lubricating base oils may range up to 15 650 °C, preferably up to 600 °C. It will be appreciated that the above boiling points and boiling point ranges refer to boiling point (ranges) at atmospheric pressure. At least a part of this hydrocarbon product is subjected to the hydroconversion step of the process of this invention, to yield the waxy raffinate. If desired, the entire effluent of the hydrogenation stage may be led directly to the hydroconversion stage. However, it 20 is preferred to separate the low molecular weight hydrocarbons, especially the C₄- fraction, from the higher molecular weight hydrocarbons prior to the hydroconversion stage. The separation may be conveniently achieved using distillation techniques well known in the art. At least a part of the remaining C₅ + fraction of the hydrocarbon product is then used as feed for the hydroconversion stage.

In the hydroconversion stage, waxy raffinate is prepared from the hydrocarbon product of the 25 hydrogenation stage by hydrocracking and hydroisomerising the product with hydrogen in the presence of a suitable catalyst. Typically, the catalyst comprises as catalytically active component one or more metals selected from Groups VIB and VIII of the Periodic Table of Elements, in particular one or more metals selected from molybdenum, tungsten, cobalt, nickel, ruthenium, iridium, osmium, platinum and palladium. Preferably, the catalyst comprises one or more metals selected from nickel, platinum and palladium as the 30 catalytically active component. Catalysts comprising platinum as the catalytically active component have been found to be particularly suitable for use in the hydroconversion stage.

Catalysts for use in the hydroconversion stage typically comprise a refractory metal oxide as a carrier. Suitable carrier materials include silica, alumina, silica-alumina, zirconia, titania and mixtures thereof. Preferred carrier materials for inclusion in the catalyst for use in the process of this invention are silica, 35 alumina and silica-alumina. A particularly preferred catalyst comprises platinum supported on a silica-alumina carrier. If desired, the acidity of the catalyst carrier may be enhanced by applying a halogen moiety, in particular fluorine, or a phosphorous moiety to the carrier. This may be especially preferred if the catalyst carrier itself is not acidic, for example if the catalyst carrier contains alumina or silica.

The catalyst may comprise the catalytically active component in an amount of from 0.05 to 80 parts by 40 weight, preferably from 0.1 to 70 parts by weight, per 100 parts by weight of carrier material. The amount of catalytically active metal present in the catalyst will vary according to the specific metal concerned. A particularly preferred catalyst for use in the hydroconversion stage comprises platinum in an amount in the range of from 0.05 to 2 parts by weight, more preferably from 0.1 to 1 parts by weight, per 100 parts by weight of carrier material.

Suitable catalysts for use in the hydroconversion stage of the process of this invention are available 45 commercially, or may be prepared by methods well known in the art, for example the methods discussed hereinbefore with reference to the preparation of the hydrocarbon synthesis catalyst.

In the hydroconversion stage of this process, the hydrocarbon product of the hydrogenation stage is 50 contacted with hydrogen in the presence of the catalyst at elevated temperature and pressure. Typically, the temperatures necessary to yield the waxy raffinate will lie in the range of from 175 to 380 °C, preferably from 250 to 350 °C, more preferably from 250 to 330 °C. The pressure typically applied ranges from 10 to 250 bars, more preferably from 25 to 250 bars. Hydrogen may be supplied at a gas hourly space velocity of from 100 to 10000 Ni/l/hr, preferably from 500 to 5000 Ni/l/hr. The hydrocarbon feed may be provided at a weight hourly space velocity of from 0.1 to 5 kg/l/hr, preferably from 0.25 to 2 kg/l/hr. The 55 ratio of hydrogen to hydrocarbon feed may range from 100 to 5000 Ni/kg and is preferably from 250 to 2500 Ni/kg.

As discussed hereinbefore in connection with the hydrogenation stage, the degree of hydrocracking and isomerisation occurring in the hydroconversion stage may be measured by determining the degree of

conversion of the fraction boiling above 370 °C, as hereinbefore defined. Typically, the hydroconversion stage is operated at a conversion of at least 20%, preferably at least 25%, but preferably not more than 50%, more preferably not more than 45%.

The hydrogen required for the operation of both the hydrogenation and the hydroconversion stages 5 may be generated by processes well known in the art, for example by the steam reforming of a refinery fuel gas.

The waxy raffinate is then subjected to a pour point reducing treatment to reduce the pour point to at least -12 °C, preferably at least -18 °C, more preferably at least -24 °C.

Pour point reducing treatments are well known to those skilled in the art and include solvent dewaxing, 10 catalytic dewaxing, (hydro) isomerisation (dewaxing) and/or addition of pour point depressing agents. The latter treatment is generally not preferred in the preparation of lubricating base oils as additives contained in a base oil may deteriorate rather quickly and blending of different base oils and additive packages to prepare a finished base oil may become a problem.

Catalytic dewaxing is well known to those skilled in the art. In a catalytic dewaxing process straight 15 chain paraffins and slightly branched paraffins are cracked to products boiling below the lubricating base oil boiling point range. However, the catalysts which are employed are not fully selective to wax molecules only. In fact also branched paraffins having a very high VI and a sufficiently low pour point are cracked to lower boiling products. Thus, cracking of those compounds to products boiling below the lubricating base oil range results in lubricating base oils having a lower VI than lubricating base oils which have been prepared 20 by a solvent dewaxing process. Further, as compared with solvent dewaxing, lubricating base oils are prepared in lower yield. Nevertheless, catalytic dewaxing is being applied commercially as generally the operation of the process is cheaper than operation of a solvent dewaxing process.

Catalysts which can be used in a catalytic dewaxing process include zeolites having a constraint index from 1 to 12, in particular of the MFI structure type, such as ZSM-5, -11, -22, -23, -35 as well as Ferrierite 25 and composite crystalline silicates described in European patent application Nos. 0 100 115, 0 178 699 and 0 380 180. Another suitable catalytic dewaxing catalyst comprises mordenite. If desired, waxy raffinate feed can be separated into various fractions and the various fraction can then be treated separately using different dewaxing catalysts, as disclosed in European patent application No. 0 237 655 and also European 30 patent application No. 0 161 833. The catalysts typically contain at least one catalytically active metal chosen from Groups VIb, VIIb and VIII of the Periodic Table of the Elements.

The catalytic dewaxing process is typically carried out at a temperature from 200 °C to 500 °C, a hydrogen pressure from 5 to 100 bar, a space velocity from 0.1 to 5 kg/l/h and a hydrogen/oil ratio from 100 to 2500 Nl/kg.

Solvent dewaxing is well known to those skilled in the art and involves admixture of one or more 35 solvents and/or wax precipitating agents with waxy raffinate and cooling the mixture to a temperature in the range of from -10 °C to -40 °C, preferably in the range of from -20 °C to -35 °C, to separate the wax from the oil. The oil containing the wax is usually filtered through a filter cloth which can be made of textile fibres, such as cotton; porous metal cloth; or cloth made of synthetic materials.

Examples of solvents which may be employed in the solvent dewaxing process are C₃-C₆ ketones (e.g. 40 methyl ethyl ketone, methyl isobutyl ketone and mixtures thereof), C₆-C₁₀ aromatic hydrocarbons (e.g. toluene), mixtures of ketones and aromatics (e.g. methyl ethyl ketone and toluene), autorefrigerative solvents such as liquefied, normally gaseous C₂-C₄ hydrocarbons such as propane, propylene, butane, butylene and mixtures thereof. Mixtures of methyl ethyl ketone and toluene or methyl ethyl ketone and methyl isobutyl ketone are generally preferred.

The solvents may be recovered from the wax and the lubricating base oil by filtration and recirculation 45 of the solvents into the process. It will be appreciated that although solvents are recirculated the process is still rather expensive as a large amount of solvents is required and cooling of the waxy raffinate/solvent mixture requires much energy.

The wax that is separated in the solvent dewaxing process may be recycled to the hydroconversion 50 stage, or alternatively, may be sent to a hydroisomerisation stage if for example, the pour point reducing treatment involves both a solvent dewaxing stage and a hydroisomerisation stage. The wax may be subjected to a deoiling treatment prior to recycling. Another possibility is to fractionate the wax and sell one or more of the fractions on the wax market. Fractionation is typically effected using short path distillation.

A very suitable pour point reducing treatment comprises a hydroisomerisation treatment, in the art 55 sometimes referred to as isomerisation dewaxing or iso-dewaxing. The hydroisomerisation treatment typically comprises contacting the waxy raffinate with hydrogen in the presence of a hydroisomerisation catalyst. As compared with a solvent dewaxing treatment the hydroisomerisation treatment is cheaper to operate and the hydroisomerisation treatment does substantially not suffer from the disadvantages of

catalytic dewaxing, that is a lower VI and a lower yield as compared with solvent dewaxing. In the hydroisomerisation process straight chain paraffins are isomerised to branched paraffins boiling within the lubricating base oil boiling point range, still having a high VI but also a low pour point. It will be appreciated that whilst hydroisomerisation reactions are preferred, hydrocracking reaction need to be avoided as much as possible. The conversion of products boiling above 370 °C to products boiling below 370 °C typically is 5 less than 25%, preferably less than 20%. The conversion is usually more than 10%.

Thus, preferably a hydroisomerisation catalyst is used having a high activity for catalysing hydroisomerisation reactions, but a low activity for catalysing hydrocracking reactions. It has been found that in order to achieve this the acidity of the catalyst, as expressed by the alpha value, should be below 10. Preferably the catalyst comprises a molecular sieve. Accordingly, in a preferred embodiment the 10 hydroisomerisation catalyst comprises a molecular sieve having an alpha value below 20, more preferably below 10, even more preferably below 5. The experimental conditions of the alpha test to be used to determine the alpha values referred to in this specification include a constant temperature of 538 °C and a variable flow rate as described in detail in *J. Catalysis*, 61, 395 (1980).

15 In one embodiment of the invention, the molecular sieve operating in hydroisomerisation duty, is a zeolite, preferably having a silica/alumina molar ratio of at least 10, more preferably at least 30. A zeolite having a high silica/alumina ratio generally has a lower acidity than a zeolite having a low silica/alumina ratio. A high silica/alumina ratio may be obtained by synthesis of the zeolite at a high silica/alumina ratio and/or by a dealumination treatment such as steaming. Both methods are well known to those skilled in the 20 art. Alternatively, framework aluminium may be replaced by another trivalent element such as boron which results in a lower level of acidity.

25 Preferably, the molecular sieve is chosen from the group of ZSM-12, mordenite and zeolite beta, more preferably zeolite beta. The low acidity forms of zeolite beta may be obtained by synthesis of a highly siliceous form of the zeolite, e.g. with a silica/alumina ratio above 50 or by steaming zeolites of lower silica-alumina ratio to the requisite acidity level. Another method is by replacement of a portion of the framework 30 aluminium of the zeolite with another trivalent element such as boron. Preferably, the zeolite contains framework boron, typically at least 0.1% by weight, preferably, at least 0.5% by weight. The zeolite also may contain material in the pores of the structure which do not form part of the framework constituting the characteristic structure of the zeolite. The term "framework boron" as used herein refers to boron that is actually present in the framework of the zeolite. As opposed to material present in the pores of the zeolite, framework boron contributes to the ion exchange capacity of the zeolite.

35 Methods for preparing zeolites having a high silica/trivalent metal ratio and containing framework boron have been described in United States patent Nos. 4 269 813 and 4 672 049. Typically, zeolite beta to be used in the process of the present invention contains at least 0.1% by weight. The boron content will usually be not more than 5% by weight, preferably not more than 2% by weight. The silica/alumina ratio of the as-synthesized zeolite is typically below 30. Preferably, the boron containing zeolite is steamed to reduce the alpha value to not more than 10, preferably not more than 5. Typical steaming conditions are known and have been described in European patent application No. 0 464 547.

40 The zeolite will usually be composited with a matrix material (binder) to form the finished catalyst. Non-acidic refractory oxide binder materials like silica, titania or alumina are preferred. Silica is especially preferred. The zeolite is usually composited with the matrix in amounts from 20 to 80% by weight, preferably from 50 to 80% by weight. Methods for extruding zeolite with the binder are known to those skilled in the art.

45 In another embodiment of the invention the molecular sieve is an aluminophosphate. Aluminophosphates are well known in the art and have been described in, for example, United States patent Nos. 4 310 440, 4 440 871, 4 567 029, and 4 793 984. Aluminophosphates have the advantage of an intrinsically lower acidity as compared with zeolites.

50 For the purposes of this specification reference to aluminophosphates is to be understood as reference to the class of aluminophosphates, that is including metallo-aluminophosphates, silico-aluminophosphates, metallo-silico-aluminophosphates as well as non-metal substituted aluminophosphates and silico-aluminophosphates.

55 Preferably, the molecular sieve has at least some intrinsic acidity and therefore the aluminophosphate is chosen from the group of metallo-aluminophosphates, wherein the further metal present in the framework of the aluminophosphate is not a trivalent metal, silico-aluminophosphates or metallo-silico-aluminophosphates.

55 In a particularly preferred embodiment the aluminophosphate is a silico-aluminophosphate.

55 In one embodiment, the process is preferably carried out with a hydroisomerisation catalyst comprising an aluminophosphate, in particular a silico-aluminophosphate, chosen from the group of structure types 11, 31 and 41, more preferably structure type 11. Silico-aluminophosphates of structure types 11, 31 and 41

have been described in international patent application No. WO 90/09362. In a particular preferred embodiment of the invention, the hydroisomerisation catalyst comprises a silico-aluminophosphate of structure type 11, and having a special silica/alumina distribution over the crystalline particle. In particular, the silico-aluminophosphate molecular sieve is characterised by an X-ray diffraction pattern according to 5 Table I.

TABLE I

	d _{hkl}	I/I ₀ * 100
10	9.41-9.17	m
	4.37-4.31	m
15	4.23-4.17	vs
	4.02-3.99	m
	3.95-3.92	m
20	3.84-3.81	m-s
	m = 20-70	
	s = 70-90	
	vs = 90-100	

25 wherein I/I₀ * 100 is the relative intensity, where I₀ is the intensity of the strongest line, and d is the interplanar spacing in angstroms corresponding to the recorded lines. X-ray powder diffraction patterns can be determined by standard techniques, using K-alpha/doublet copper radiation.

30 The silico-aluminophosphate is further characterised by a P₂O₅ to alumina molar ratio at the surface of 0.80 or less and a P₂O₅ to alumina ratio of the bulk of the silico-aluminophosphate is 0.96 or greater, and the silica to alumina mole ratio at the surface is greater than in the bulk of the silico-aluminophosphate. This silico-aluminophosphate is known in the art as SM-3. Preparation of SM-3 has been disclosed in international patent application No. WO 91/13132.

35 In yet another embodiment of the invention, the isomerisation catalyst comprises an inorganic, non-layered, porous, crystalline phase material as described in international patent application No. WO 93/02161.

40 The hydroisomerisation catalyst typically comprises a catalytically active metal having hydrogenation/dehydrogenation activity, such as those of Groups VIb and VIII. Preferably, the hydroisomerisation catalyst comprises a Group VIII metal, in particular a Group VIII noble metal such as platinum and/or palladium. Means for incorporating the metal into the catalyst carrier, comprising a molecular sieve as described hereinbefore, are well known to those skilled in the art and have been described hereinbefore. The amount of noble metal is typically in the range of from 0.5 to 5% by weight of the total catalyst, preferably in the range of from 0.5 to 2% by weight.

45 In the hydroisomerisation stage of this process, the waxy raffinate is contacted with hydrogen in the presence of a catalyst as described hereinabove at elevated temperature and pressure. Typically, the temperatures necessary to yield the lubricating base oil will lie in the range of from 175 to 380 °C, preferably from 200 to 350 °C. The pressure typically applied ranges from 10 to 250 bars, more preferably from 25 to 250 bars. The waxy raffinate may be provided at a weight hourly space velocity of from 0.1 to 20 kg/l/hr, preferably from 0.1 to 5 kg/l/hr.

50 The finished lubricating base oil preferably has a pour point of less than -15 °C, more preferably less than -20 °C and a VI of more than 135, preferably more than 140. Preferably, it should not be necessary to treat the hydrogenated hydroconverted hydroisomerised lubricating base oil with an additional pour point reducing treatment. However, it may be desired to isomerise the waxy raffinate to an intermediate pour point and solvent dewax the isomerized waxy raffinate to the final pour point.

55 **Claims**

1. A process for the preparation of lubricating base oils comprising subjecting a waxy raffinate to a pour point reducing treatment, and recovering a lubricating base oil therefrom, which waxy raffinate has been prepared by contacting a hydrocarbon product with hydrogen in the presence of a hydroconversion

catalyst, comprising a catalytically active metal having hydrogenation/dehydrogenation activity supported on a refractory oxide carrier, under conditions such that hydrocracking and hydroisomerisation of the hydrocarbon product occur to yield the waxy raffinate, wherein the hydrocarbon product has been prepared by:

5 (a) contacting a mixture of carbon monoxide and hydrogen with a hydrocarbon synthesis catalyst at elevated temperature and pressure to prepare a substantially paraffinic hydrocarbon wax; and
 (b) contacting the hydrocarbon wax so-obtained with hydrogen in the presence of a hydrogenation catalyst under conditions such that substantially no isomerisation or hydrocracking of the hydrocarbon wax occurs to yield the hydrocarbon product.

10 2. A process as claimed in claim 1, characterised in that the mixture of carbon monoxide and hydrogen contacting the catalyst in step (a) has a hydrogen/carbon monoxide ration of less than 2.5, preferably less than 1.75, more preferably of from 0.4 to 1.5.

15 3. A process as claimed in either of claims 1 or 2, characterised in that the hydrocarbon synthesis catalyst in step (a) comprises ruthenium, iron, nickel or cobalt as a catalytically active metal, preferably cobalt.

20 4. A process as claimed in any preceding claim, characterised in that the hydrocarbon synthesis catalyst in step (a) comprises a carrier, preferably selected from silica, alumina, titania, zirconia, and mixtures thereof, most preferably silica or alumina.

25 5. A process as claimed in any preceding claim, characterised in that the hydrocarbon synthesis catalyst in step (a) comprises as a promoter an oxide of a metal selected from Group IVB of the Periodic Table of the Elements, promoter an oxide of a metal selected from Group IVB of the Periodic Table of the Elements, preferably titanium or zirconium.

30 6. A process as claimed in any preceding claim, characterised in that the mixture of carbon monoxide and hydrogen is contacted with the catalyst in step (a) at a temperature of from 125 to 300 °C, preferably from 175 to 250 °C.

35 7. A process as claimed in any preceding claim, characterised in that the mixture of carbon monoxide and hydrogen is contacted with the catalyst in step (a) at a pressure of from 5 to 100 bars, preferably from 12 to 50 bars.

40 8. A process as claimed in any preceding claim, characterised in that the hydrogenation catalyst of step (b) comprises molybdenum, tungsten, cobalt, nickel, ruthenium, iridium, osmium, platinum or palladium as a catalytically active metal, preferably one or more of nickel, platinum and palladium.

45 9. A process as claimed in any preceding claim, characterised in that the hydrogenation catalyst of step (b) comprises a carrier, preferably selected from silica, alumina, silica-alumina, titania, zirconia and mixtures thereof, preferably silica, alumina or silica-alumina.

50 10. A process as claimed in any preceding claim, characterised in that in step (b) the hydrocarbon product is contacted with the hydrogenation catalyst at a temperature of from 100 to 300 °C, preferably from 150 to 275 °C.

55 11. A process as claimed in any preceding claim, characterised in that in step (b) the hydrocarbon product is contacted with the hydrogenation catalyst at a pressure of from 5 to 150 bars, preferably from 10 to 50 bars.

60 12. A process as claimed in any preceding claim, characterised in that in step (b) hydrogen is provided at a gas hourly space velocity of from 100 to 10000 Nl/l/hr, preferably from 250 to 5000 Nl/l/hr.

65 13. A process as claimed in any preceding claim, characterised in that in step (b) the conversion is below 10%, more preferably below 5%.

70 14. A process as claimed in any preceding claim, characterised in that the hydroconversion catalyst comprises molybdenum, tungsten, cobalt, nickel, ruthenium, iridium, osmium, platinum or palladium as

a catalytically active metal, preferably one or more of nickel, platinum and palladium.

15. A process as claimed in any preceding claim, characterised in that the hydroconversion catalyst comprises a carrier, preferably selected from silica, alumina, silica-alumina, titania, zirconia and mixtures thereof, preferably silica, alumina or silica-alumina.
5
16. A process as claimed in claim 15, characterised in that the hydroconversion catalyst comprises a halogen-containing carrier.
10
17. A process as claimed in any preceding claim, characterised in that the hydrocarbon product is contacted with the hydroconversion catalyst at a temperature of from 175 to 380 °C, preferably from 250 to 350 °C.
15
18. A process as claimed in any preceding claim, characterised in that the hydrocarbon product is contacted with the hydroconversion catalyst at a pressure of from 10 to 250 bars, preferably from 25 to 250 bars.
15
19. A process as claimed in any preceding claim, characterised in that in the hydroconversion step hydrogen is provided at a gas hourly space velocity of from 100 to 10000 NL/l/hr, preferably from 500 to 20 5000 NL/l/hr.
20
20. A process as claimed in any preceding claim, characterised in that in the hydroconversion step the conversion is at least 20%.
25
21. A process as claimed in any preceding claim, characterised in that the pour point reducing treatment comprises contacting the waxy raffinate with hydrogen in the presence of a hydroisomerisation catalyst.
25
22. A process as claimed in claim 21, characterised in that the hydroisomerisation catalyst comprises a molecular sieve and the catalyst has an alpha value below 20, preferably below 10.
30
23. A process as claimed in claim 22, characterised in that the molecular sieve is a zeolite, preferably having a silica/alumina molar ratio of at least 10.
35
24. A process as claimed in claims 22 or 23, characterised in that the molecular sieve is chosen from the group of ZSM-12, mordenite and zeolite beta, preferably zeolite beta.
35
25. A process as claimed in claim 22, characterised in that the molecular sieve is an aluminophosphate.
40
26. A process as claimed in claim 25, characterised in that the aluminophosphate is a silico-aluminophosphate.
40
27. A process as claimed in claim 25 or 26, characterised in that the aluminophosphate is chosen from the group of structure types 11, 31 and 41, preferably structure type 11.
45
28. A process as claimed in any one of the preceding claims, characterised in that the hydroisomerisation catalyst comprises a catalytically active metal selected from Groups VI B and/or VIII of the Periodic Table of the Elements, preferably one or more Group VIII noble metals.
45
29. A process as claimed in any one of the preceding claims, characterised in that the pour point reducing treatment comprises a solvent dewaxing treatment or a catalytic dewaxing treatment.
50
30. A lubricating base oil whenever prepared by a process as claimed in any preceding claim.
55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 20 0281

DOCUMENTS CONSIDERED TO BE RELEVANT													
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim											
X	EP-A-0 323 092 (EXXON) * claims 1,2,5,6,8 * * page 2, line 15 - line 20 * ---	1,3,8,9, 11,12, 14-20, 29,30											
D,P, A	EP-A-0 583 836 (SHELL INT RESEARCH) 23 February 1994 * claims 1-19 * ---	1-15, 17-20											
A	EP-A-0 464 546 (MOBIL) 8 January 1992 * claims 1,4-6 * * example 1 * -----	1,21-24											

<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="padding: 2px;">CLASSIFICATION OF THE APPLICATION (Int.Cl.6)</td> </tr> <tr> <td style="padding: 2px;">C10G65/04</td> </tr> <tr> <td colspan="2" style="text-align: center; padding: 2px;">TECHNICAL FIELDS SEARCHED (Int.Cl.6)</td> </tr> <tr> <td colspan="2" style="text-align: center; padding: 2px;">C10G</td> </tr> </table>			CLASSIFICATION OF THE APPLICATION (Int.Cl.6)	C10G65/04	TECHNICAL FIELDS SEARCHED (Int.Cl.6)		C10G						
CLASSIFICATION OF THE APPLICATION (Int.Cl.6)													
C10G65/04													
TECHNICAL FIELDS SEARCHED (Int.Cl.6)													
C10G													
The present search report has been drawn up for all claims													
Place of search	Date of completion of the search	Examiner											
THE HAGUE	7 June 1995	De Herdt, O											
<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="padding: 2px;">CATEGORY OF CITED DOCUMENTS</td> </tr> <tr> <td style="padding: 2px;">X : particularly relevant if taken alone</td> </tr> <tr> <td style="padding: 2px;">Y : particularly relevant if combined with another document of the same category</td> </tr> <tr> <td style="padding: 2px;">A : technological background</td> </tr> <tr> <td style="padding: 2px;">O : non-written disclosure</td> </tr> <tr> <td style="padding: 2px;">P : intermediate document</td> </tr> <tr> <td style="padding: 2px; text-align: right;">T : theory or principle underlying the invention</td> </tr> <tr> <td style="padding: 2px; text-align: right;">E : earlier patent document, but published on, or after the filing date</td> </tr> <tr> <td style="padding: 2px; text-align: right;">D : document cited in the application</td> </tr> <tr> <td style="padding: 2px; text-align: right;">L : document cited for other reasons</td> </tr> <tr> <td style="padding: 2px; text-align: right;">& : member of the same patent family, corresponding document</td> </tr> </table>			CATEGORY OF CITED DOCUMENTS	X : particularly relevant if taken alone	Y : particularly relevant if combined with another document of the same category	A : technological background	O : non-written disclosure	P : intermediate document	T : theory or principle underlying the invention	E : earlier patent document, but published on, or after the filing date	D : document cited in the application	L : document cited for other reasons	& : member of the same patent family, corresponding document
CATEGORY OF CITED DOCUMENTS													
X : particularly relevant if taken alone													
Y : particularly relevant if combined with another document of the same category													
A : technological background													
O : non-written disclosure													
P : intermediate document													
T : theory or principle underlying the invention													
E : earlier patent document, but published on, or after the filing date													
D : document cited in the application													
L : document cited for other reasons													
& : member of the same patent family, corresponding document													